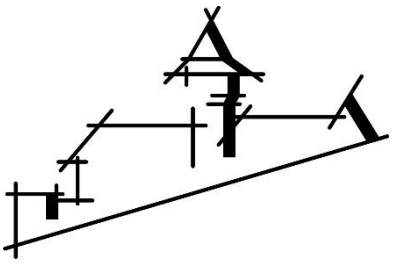
PROGRESSIVE TRENDS IN COORDINATION, BIOINORGANIC, AND APPLIED INORGANIC CHEMISTRY



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Effect of Na-citrate on the precipitation of gypsum from highly supersaturated solutions

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Gypsum precipitation causes a lot of technological complications through scaling in pipes and precipitating in oil drillings and wells. Therefore, the inhibition of the gypsum precipitation is of significant practical importance. In this work the effect of Na-citrate on gypsum precipitation has been investigated, with regard to changes in reaction kinetics and in the morphology of the precipitated solid. The gypsum was precipitated *via* reacting Na_2SO_4 and $CaCl_2$ at high supersaturation and agitating the reaction mixture at high speed, speeding up the precipitation with both conditions. Na-citrate significantly slowed down both the nucleation and the crystal growth. The reactions were monitored simultaneously by conductometry as well as by direct potentiometry using Ca-ISE. The precipitated solids were studied by powder XRD and SEM to investigate the changes of morphology.

INTRODUCTION

The unwanted precipitation of gypsum, $CaSO_4 \cdot 2H_2O$ can cause technological hardships in a lot of areas. Gypsum crystallizes as a side product during the production of phosphoric acid, and the control of the crystal size and morphology can be crucial during filtration. The precipitation of gypsum in pipes of sewage systems or agricultural watering systems can cause clogging. In oil and gas wells it is one of the major scales, causing a large variety of technological problems.

The crystal growth of gypsum was studied by introducing crystal seeds to supersaturated solutions. This way, the growth and nucleation can be studied separately. There are several studies regarding this area, focusing on the mechanism of the crystal growth [1-4]. However, the results are slightly different, probably due to reaction's strong dependence of the seeds quality [5-7] and the reaction conditions [8]. The crystal growth was also investigated together with nucleation at various conditions, for example at constant $[Ca^{2+}]$ [9], at constant conductivity [10] and with various techniques such as optical monitoring [11] and QCM [12]. These studies yielded some basic understanding of the effect of different additives on the crystallization.

The inhibition of gypsum crystallization was studied first in the late 1950's [13]. The authors studied the effect of different types of additives to get information about the chemical nature of compounds that can behave effectively as inhibitor [13]. Various compounds were found to be effective inhibitors of the precipitation of gypsum; the most efficient ones were phosphonates [14, 15] and polycarboxylates [16, 17]. The strong inhibition effect is suspected to be due to the ability of these species to strongly bind on the surfaces of the crystal embryos, thus prohibiting the growth of the crystals. By binding to the surface before the particles could reach the critical size of nucleation, they can keep the solution in metastable state for a significant amount of time.

Comparing the common polycarboxylates we can see, that citrate ion is outstanding in this area [16]. It is a commonly available and relatively cheap material, therefore, a lot of studies engage in the investigation of its inhibitory behavior. Its effect on the nucleation of gypsum (from mixing Na_2SO_4 and $CaCl_2$ solutions) was investigated by turbidity measurements varying the initial reactant concentration and ratio [18, 19]. The inhibition effect of citric acid was also studied in the presence of different transition metal ions [20]. The phenomenon was even tested in the context of scaling of gypsum in pipes [21], and the reaction at higher supersaturation [22, 23]. The available studies have a lot of information about the inhibition effect of citrate ion on the precipitation of gypsum, the experiments are often carried out at elevated temperatures, at not too high supersaturation and at slightly acidic pH (this way the inhibiting citrate anion is to some extent protonated).

The aim of this study was to investigate the inhibiting ability of citrate ions on gypsum precipitation. The solid was obtained from the reaction of Na_2SO_4 and $CaCl_2$ at high gypsum supersaturation and the system was agitated at high speed; both conditions aid. The effect of Na-citrate in slowing the nucleation and crystal growth was then studied. The reactions were monitored by conductometry and as an alternative measuring method, Ca-ISE. The precipitated solids were characterized in terms of changes in morphology and composition too.

EXPERIMENTAL PART

Reagents and solutions

Gypsum was precipitated from the following reaction:

$$CaCl_2 + Na_2SO_4 + 2\ H_2O \rightarrow 2\ NaCl + CaSO_4 \cdot 2H_2O$$

The reaction was carried out by mixing two solutions containing equivalent amounts of reactants. The initial Ca^{2+} and SO_4^{2-} concentration in the reaction mixture was 0.1 M. The solutions were prepared by dissolving anhydrous $CaCl_2$ and Na_2SO_4 salts in distilled water. To ensure the absence of crystalline water, the salts were kept at 120°C for 24 hours, and the solutions were made up right after this treatment to prevent the uptake of water from the air. To inhibit the reactions, different amounts of Na-citrate-dihydrate was dissolved in the Na_2SO_4 reactant solution, varying the citrate concentration between 0.5 mM and 5 mM. All the salts listed above were products of VWR.

The reaction was carried out in a cylindrical PTFE vessel to have minimal wall-effect possible. The total reaction volume was 100 mL. The system was agitated by magnetic stirring with 300 rpm speed to completely homogenize the fluid. The reactions were followed by *in-situ* conductometric measurements and simultaneously with Ca-ISE. To have better control and repeatability of the reactions, always the same stirring equipment was used, and the positioning of the electrodes was also unchanged from run to run. The pH of the reactions was also determined at different times, to check if practically all of the carboxylic groups of the citrate are deprotonated, thus enhancing its capability to coordinate to the crystal surface.

When the precipitation reactions reached the equilibrium, the solids were filtered by vacuum filtration and dried at 60°C. The $[Ca^{2+}]$ of the filtrate was measured by titration with EDTA solutions using murexide indicator.

From the results of the *in-situ* measurements the variation of $[Ca^{2+}]$ was calculated presuming that the change of signal was proportional to the variation of $[Ca^{2+}]$ in case of conductivity and to the $\lg[Ca^{2+}]$ in case of Ca-ISE.

The precipitated solid was studied by powder XRD and SEM measurements to follow the morphological changes of gypsum caused by citrate.

Apparatus and equipment

For conductivity measurements a Jenway 3540 pH and conductivity meter and a Jenway 027013 conductivity cell was used.

For potentiometric measurements a Metrohm 794 Basic Titrino and a Metrohm combined Ca-ISE was used.

The pH measurements were carried out using Jenway 3540 pH and conductivity meter and Sentix 62 pH electrode.

Powder X-ray diffractograms were measured using Rigaku MiniFlex II type Röntgen diffractometer.

SEM images were captured with a Hitachi S-4700 scanning electron microscope.

RESULTS AND DISCUSSION

The precipitation of gypsum was studied during stochiometric reactions of Na_2SO_4 and $CaCl_2$ with initial reactant concentration of 0.1 M. The reactions were constantly agitated by magnetic stirring (300 rpm). Na-citrate was tested as crystallization inhibitor; its effect on the reaction kinetics is shown on Fig 1.

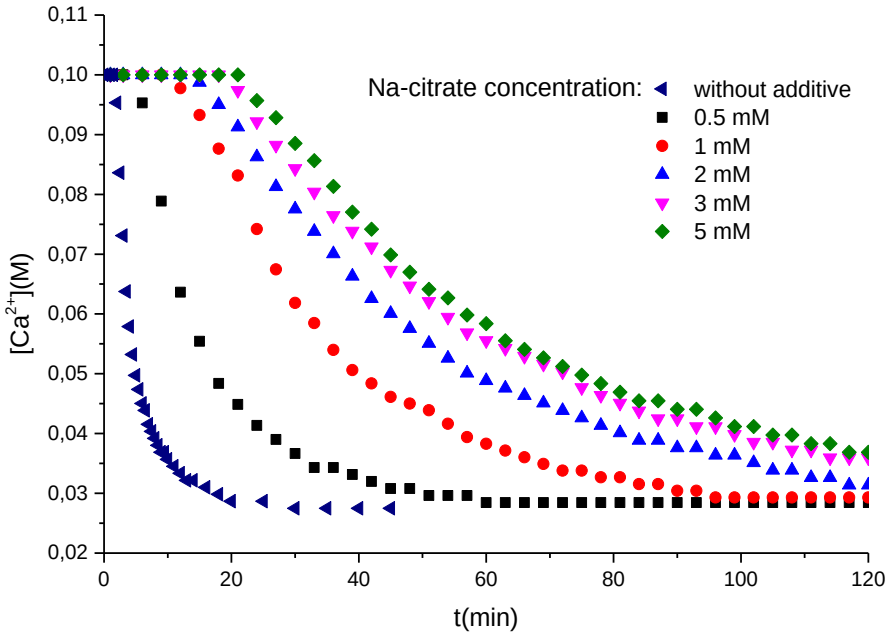

Figure 1. Variation of $[Ca^{2+}]$ calculated from conductometric measurements during the reaction of $CaCl_2$ and Na_2SO_4 with 0.1 M initial reactant concentration, varying the amount of added Na-citrate.

It can be seen that even at as low inhibitor concentration as 0.5 mM, relative to the inhibitor-free case the induction time became significantly longer, and the rate of crystal growth is also decreased. However, by raising the citrate concentration, the inhibiting effect does not grow proportionally. At citrate concentrations higher than 2.5-3 mM, the further increase of citrate concentration does not cause further substantial changes in the reaction kinetics: mainly the crystal growth is slowed further

but the induction time changes only slightly. This can be because the surfaces of the small nuclei below the critical nucleation size are almost fully covered by the citrate anions; therefore, the access of citrate cannot cause further change in the induction of the precipitation.

When conductometry is employed to monitor the progression of the precipitation reaction, certain inherent limitations are needed to be taken into account. At high electrolyte concentrations the signal may not be exactly linearly proportional to the electrolyte concentration. Moreover, at high background electrolyte concentrations the effect caused by the precipitation reaction can be swamped by the high background conductivity. Ca-ISE can be a viable alternative under these conditions, because the high concentration of background electrolyte results in approximately constant ionic strength, which is a prerequisite for the stable Ca-ISE signal. However, the response time of Ca-ISE is much slower than that of the conductometric electrode; therefore Ca-ISE is suitable to monitor only sufficiently slow precipitation reactions. This is well demonstrated in Fig 2.

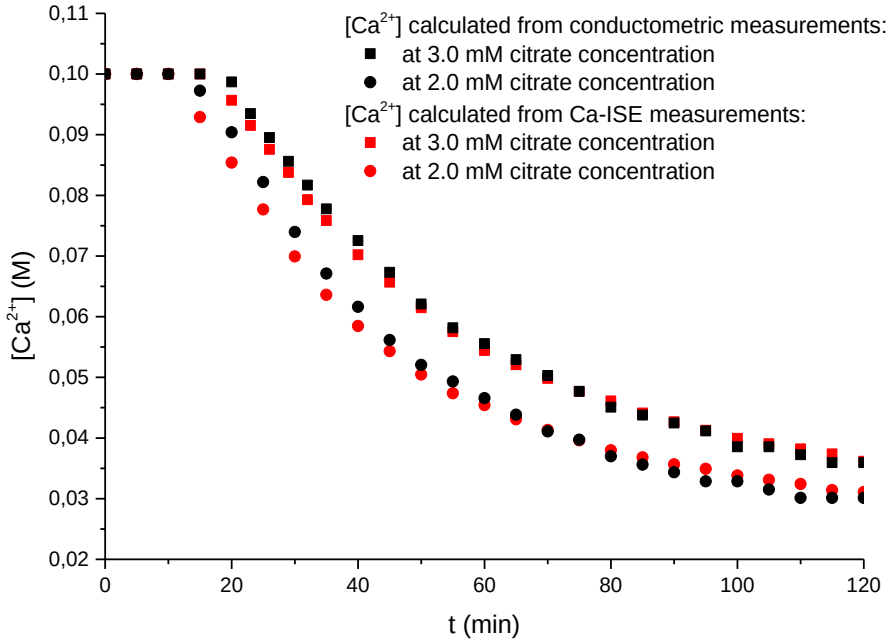

Figure 2. Comparison of the conductometric and Ca-ISE potentiometric measurement results in the precipitation reaction of gypsum inhibited by various amounts of Na-citrate.

The precipitated solids were studied by powder XRD measurements to determine the composition of the crystals, and to investigate the effect of the addition of citrate anions to the reactions. The comparison of the solids precipitated from citrate-free systems and the ones in the presence of citrate are shown on Fig. 3. Because no significant changes were found at different citrate concentrations, only two diffractograms are shown here.

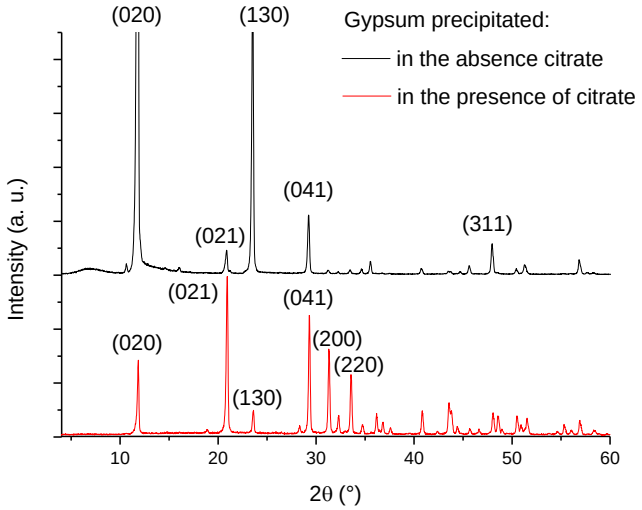

Figure 3. Diffractograms of gypsum precipitated in the absence and in the presence of citrate anions (reflections were identified using JCPDS database, the peak of (020) plane is truncated for better visualization).

The only solid we could identify (using JCPDS database) in the precipitates was $CaSO_4 \cdot 2H_2O$ (gypsum); no other forms (anhydrous or hemihydrate) occurred. It can be seen, that reflection intensities of the different planes exhibit significant differences when XRDs of gypsum precipitated in presence and in absence of citrate are compared. This gives us an explanation on the remarkable inhibiting effect of citrate. The drop of the sharpest reflections suggests, that the crystal faces that grow faster in absence of citrate, are covered by citrate, this way it slows the nucleation and the crystal growth drastically. The differences seen on the XRDs are also present in the morphology of the crystals. The corresponding SEM images of the different precipitates are shown on Fig. 4.

Because the reactions were agitated at high speed a lot of the crystals were broken, however we can see that the morphology of gypsum changed indeed. In the absence of citrate, rod-like features are observed, while in the presence of the additive, plates of gypsum can be seen. The size of the crystals also supports the inhibition effect of citrate. As the crystals had three-four times more time in the inhibited reactions to grow, their primary particle size (obtained from the width of the XRD reflections) is similar to those precipitated from additive-free reaction mixtures.

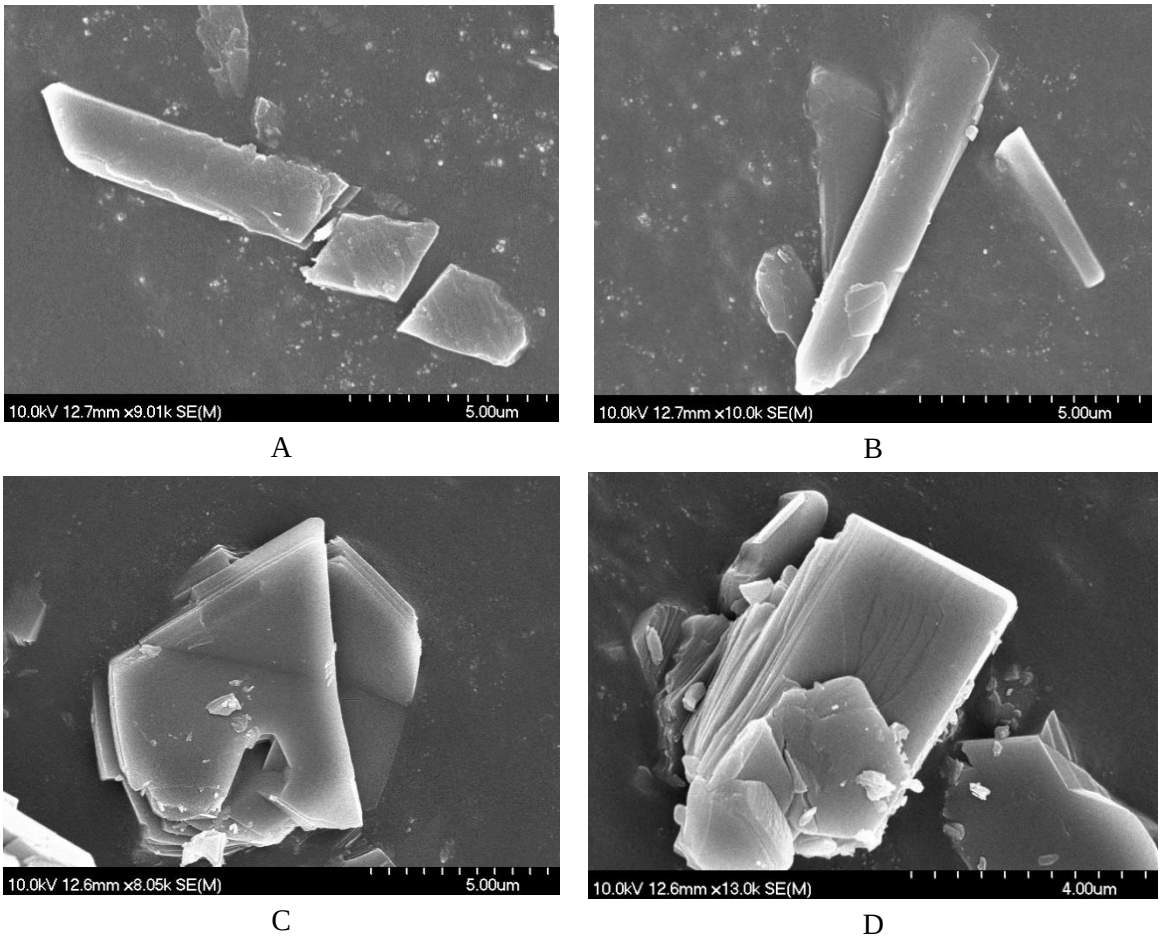

Figure 4. SEM pictures of gypsum crystals precipitated
A, B: in the absence and C, D: in the presence of citrate anions.

SUMMARY

To sum up our results, we successfully tested the inhibiting abilities of citrate anions in the precipitation of gypsum under conditions strongly facilitating the precipitation. Ca-ISE was found to be a viable method to monitor the reaction, providing that the precipitation is sufficiently slow. The changes of the precipitated solids were also studied; citrate was found to cause remarkable changes in the morphology *via* its strong interaction with certain crystal faces of gypsum.

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